DESTRUCTIVE DISTILLATION.

A MANUALETTE.

DESTRUCTIVE DISTILLATION:

A MANUALETTE

OF THE

PARAFFIN, COAL TAR, ROSIN OIL, PETROLEUM,

AND

KINDRED INDUSTRIES.

BY

EDMUND J. MILLS, D.Sc. (Lond.), F.R.S.,

"Young" Professor of Technical Chemistry in Anderson's College, Glasgow.

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PREFACE.

DESTRUCTIVE distillation is a very ancient industry, whose intricate and numerous problems have been from time to time investigated by the ablest chemists. Its study has thus had a prominent influence in developing the science of Chemistry.

This little book is the first to present as a whole the industry of destructive distillation. Its contents are the substance of a course of lectures delivered in Anderson's College, Glasgow, in 1875-76, and illustrated by actual inspection of many of the processes to which it refers. Students will profit most from its perusal who have such illustration at command; and manufacturers will, it is hoped, be interested in the modern principles of the science that underlies their processes, and reap some advantage from learning how others treat the very same problems that are presented to themselves.

The author begs to express his sincere thanks to the managers of works and other friends who with much kindness, and sometimes with much trouble, have contributed to his information on this important subject.

"YOUNG" LABORATORY OF TECHNICAL CHEMISTRY,
ANDERSON'S COLLEGE, GLASGOW.
November 1*st*, 1877.

DESTRUCTIVE DISTILLATION.

GENERAL CONSIDERATIONS.

1. DESTRUCTIVE distillation is the decomposition of a substance in a close vessel, in such a manner as to obtain liquid products.

By a *product* is meant a body not originally present in the substance distilled. A body merely extracted without change by distillation is termed an *educt*. Manufactured ozokerite consists in part of educts from the native mineral, but this is an almost singular case in the industry of destructive distillation.

2. If an extended list of substances volatile without decomposition be examined, it will be found that the numerical values of their chemical symbols, or formulæ, are, on the whole, comparatively low; while bodies that do not volatilise without decomposition have, on the whole, a comparatively high symbolic value. These laws are both comprised in the more general one—that chemical activity increases on the whole with symbolic value.

3. The apparatus employed in destructive distillation consists essentially of a *retort*, followed by a *condenser* and a *receiver*. The substance to be operated on is placed inside the retort, to which heat is applied; the volatile products pass over and are condensed in long straight or helical tubes, which are kept more or less cooled. The average contraction, from heated vapour to liquid, may be taken at about 1000: 1. The retort or still has various

forms, and may be set either in a horizontal or vertical position; in the latter case the bottom may consist of water. Its material may be glass, iron, clay, or brick. Heat is applied directly either to the sides or bottom, or both; or superheated steam alone may be driven in at one end. Steam of varied initial temperature, and direct heat, are sometimes used together.

4. The nature of the products depends (*a*) on the composition of the substance heated; (*b*) on the degree of heat applied; but (*c*) not to any serious extent (on the large scale) on the material of the retort.

(*a*.) If an organic substance contain much infusible mineral matter (as, for instance, in the case of ordinary bituminous shale, which contains a great deal of aluminic silicate), the latter will hold down the former, and compel recourse to a higher temperature. Thus gum-benzoin, when distilled alone, yields benzoate; when mixed with sand, it furnishes benzol. In cases of this kind, the fine state of division or porosity of the earthy constituent contributes, with the higher temperature, to a change in the nature of the prevailing reaction. Thus, the later products in the preparation of coal tar consist in part of dehydrogenated fatty hydrides.

The presence of chlorine, sulphur, oxygen, nitrogen, and hydrogen, in carbon compounds, gives rise to chlorides, sulphides, oxides, etc., in the distillate. Oxides generally precede hydrides in the condenser, as is strikingly seen in the destructive distillation of wood. Excepting plants known as *Cruciferæ* and the like, animal compounds give the most highly sulphurised distillate.

5. (*b*.) The nature of the decomposition which takes place on heating, is indicated by the term *cumulative resolution.* Instances of this are very common in inorganic chemistry. Thus, three units of manganic dioxide decompose in

partnership, yielding a unit of trimanganic tetroxide and a unit of oxygen;

$$3MnO_2 = Mn_3O_4 + O_2.$$

When glycerin is heated, polyglycerins are formed by the union of n units of glycerin, which lose $(n-1)$ units of water;

$$nC_3H_8O_3 - (n-1)H_2O = C_{3n}H_{6n+2}O_{2n+1}.$$

This last expression, when divided by n, becomes—

$$C_3H_{6+\frac{2}{n}}O_{2+\frac{1}{n}};$$

so that the ultimate stage of this accumulation, when n becomes indefinitely great, must be a polymer of glycide, $C_3H_6O_2$. Pursuing the same course with glycide, &c., we have the following table of results:—

Glycerin Alcoholoïds.		Extreme Accumulation.
$C_3H_8O_3$	.. ..	$nC_3H_6O_2$
$nC_3H_6O_2$	.. ..	nnC_3H_4O
nnC_3H_4O	.. ..	$nnnC_3H_2$

The above mode of resolution is common to all polyalcohols. In the important case of woody fibre (whose minimum formula is $C_6H_{10}O_5$) we have the two series—

Cellulose Alcoholoïds.		Extreme Accumulation.
$C_6H_{10}O_5$	.. ..	$nC_6H_8O_4$
$nC_6H_8O_4$	.. ..	$n^2C_6H_6O_3$
$n^2C_6H_6O_3$	.. ..	$n^3C_6H_4O_2$
$n^3C_6H_4O_2$	.. ..	$n^4C_6H_2O$
$n^4C_6H_2O$	.. ..	n^5C_6

In this manner, we eventually arrive at carbon as the result of retort operations upon wood; the gentler process of nature furnishes coal.

The preceding theory is practically modified by the law of decomposition already given. The numerical values of

the cumulative formulæ increase nearly by powers of *n*: hence the bodies represented are *pro tanto* more prone to decompose, and to vary in their kind of decomposition. Accordingly it is observed, that the number of by-products and subsidiary reactions increase, but more slowly towards the last, with the degree of heat applied. Precisely similar considerations hold good for hydrides, chlorides, and all other bodies susceptible of cumulative resolution. Hence the presence of homologous series in tars.

The process of decomposition by means of heat is most completely realised in the sun's atmosphere, which consists of the resolved weights of our common elementary, and perhaps some more simple, bodies. At the next lower temperature, that of the voltaic discharge, hydrogen unites with carbon to form acetylene, and with oxygen to form water. From these two products, most organic bodies can be obtained by synthesis: benzol, for instance, by keeping acetylene for a long time just below a red heat; naphthalin, by passing a stream of benzol or one of its homologues through a red-hot tube; ethylene, by hydrogenating acetylene; alcohol, by hydrating ethylene. Hence naphthalin, hydrogen, and acetylene, with less benzol, are found in coal-tar products when a very high temperature is used; at a dull red heat they are absent, more benzol, and chrysene, being found. At a very high temperature, the products from coal and shale are carbon, and carbonised gases of low illuminating power, with but little liquid distillate; at a low temperature, there is much liquid product, and gas of high illuminating power. The greatest amount of liquid product of low boiling-point is found in American and Russian petroleums, which have probably been produced by the long-continued application of a very gentle heat.

When coal is slowly heated (as must be to a great

extent the case when it is broken fine, or when a large retort is used), its oxygen is chiefly converted into water; when rapidly heated, the oxygen is expelled as carbonic oxides.

6. The retort was doubtless originally derived from the clay bottle, which in its turn was modelled on an animal skin, or vegetable seed-case. In the sixteenth and seventeenth centuries, destructive distillation came to be the principal work in chemical laboratories. Most animal substances—sometimes the entire body (as, for instance, of the viper)—as well as plants, were so examined, or, as it was termed, "analysed." It was, however, seldom that any detailed investigation was made of the products. These were classified, according to Lemery (1686), into five groups; *three active:* "spirit" or "mercury" (most volatile), "oil" or "sulphur" (less volatile), and "salt" (least volatile, or even fixed), soluble in water; *two passive:* "water" or "phlegm" (passing over before the spirits when they are fixed, after them when volatile), and "earth," "terra damnata" or "caput mortuum," a dry uninflammable residue. From this epoch the terms "oil" and "spirit" still survive in their ancient sense.

The phlogistic, oxygenic, and atomic periods in chemical history have not been specially characterised by attention to destructive distillation. Much light, however, has been incidentally thrown upon it by the great modern revival in organic chemistry. By a study of the reactions of a number of individual definite substances, a skeleton theory of the process has at least been rendered possible. It is in the systematic researches of Reichenbach, Runge, Stenhouse, and Anderson, in connection with destructive distillation, that the basis of all our exact knowledge is to be found; while the investigations of Gerhardt and Würtz into the behaviour of polyacids and polyalcohols

have furnished the lucid superstructure. For much suggestive work on synthesis and inverse reactions, we are indebted to Berthelot.

Coal-gas came into use in about the year 1820 as an illuminating agent. Paraffin was discovered by von Reichenbach in 1830, in beech tar. The low-temperature industry was commenced, as such, by Mr. James Young, in 1851.

7. In the process of refining crude distillates, advantage is taken of the fact that the different constituents of such mixtures boil and pass over at different temperatures. This process of separating is termed "fractional distillation," for the theory of which we are chiefly indebted to Wanklyn. In 1863, that author showed that "the quantity of each ingredient which distils will be found by multiplying its tension at the boiling-point of the mixture by its vapour-density." Thus, methylic alcohol boils at 66°, methylic iodide at 72°; but from a mixture of the two, the latter distils even in greater quantity. The liquid with the highest vapour-tension will thus not necessarily distil the quickest, for what the accompanying liquids want in tension they may make up by the greater density of the vapours they give off. If t represent tension, and d density, then, for various liquids x—

$$x_1 = k_1\, t_1\, d_1;\; x_2 = k_2\, t_2\, d_2;\; x_3 = k_3\, t_3\, d_3;\; \&c.;$$

k being a constant of condition, calculated from the experiments. If the vapour-densities and tensions are inversely proportional, and the values of k equal, the products $k_n t_n d_n$ will all be equal, and the mixture will remain unchanged in composition while distilling. Homologous bodies, that is, those members of the same series whose common difference is CH_2, are thus difficult to separate; because, though the tension sinks with each increment of CH_2, the vapour-density rises. Many oils

distil over more readily in a current of steam (one of the lightest vapours), because their vapours are usually heavy; hence one reason for the introduction of steam into paraffin retorts. Under diminished pressure, the differences between the vapour-tensions of liquids are increased, and their separation is so far facilitated; to this principle the use of exhausters in gas-works is for the most part due.*

PARAFFIN INDUSTRY.

8. Paraffin oil can be prepared from coal, bituminous shale, lignite, wood, peat, Kimmeridge clay, and the like, on the one condition that a very low red-heat is employed. The material originally used in this country was boghead coal, or the Torbanehill mineral, exhausted in 1872; this yielded 33 per cent. of tar, and 1—1½ per cent. of crude paraffin. At present, selected mid-vein shales are used, which furnish about 11 per cent. of tar, the average yield also of good foreign shales. Certain authorities, quoted by Wagner (*Technology*, pp. 687–8, 1872), give the results of the examination of forty different kinds of coal, peat, etc., as treated for low-temperature tar. The means are, omitting boghead :—

	Tar per Cent.	Sp. Gr.	Paraffin.
23 kinds	8·1	0·97	..
17 kinds	..	..	0·6 per cent.

* For a further development of the theory of fractional distillation, see Wanklyn, *Philosophical Magazine* (4), xlv, 129; and Glashan, *ibid.*, 273.

The presence of low-pressure steam increases the yield of crude tar by about 10 per cent.; much superheated steam burns the shale, and converts the ordinary alkaline into an acid distillate. The boghead tar was found comparatively difficult to purify; the present, or 11 per cent., tar is easier to purify, because the hot porous shale in the retort has itself done work of purification. (Comp. § 4.)

9. The retort is of varied form and capacity. It is constructed of thin cast iron, and may be either elliptic or circular, or semicircular in section; horizontal, or upright; narrow and tall, narrow and long, or wide and short. Preference has been given in very large works to the narrow, elliptic, upright kind. The retort is either closed by a door, screwed down and rendered tight by moist clay; or, if vertical, closed at the bottom by mere immersion in water. The latter method allows the spent shale to be cooled and removed very conveniently. The charging is intermittent. The charge fills the retort, and weighs from 1—2 cwt.; in a vertical retort, it is introduced through a hopper, closed by an iron valve, which is rendered tight by sand. 25 cwt. are generally worked off in about 24 hours; the retorts are charged every 3 hours, and drawn every hour.

Rolle's retort consists of a vertical cylinder, 16 feet high and 6 feet wide. This contains a number of very short and very open funnels, having the narrow end uppermost, and separated from the cylinder by a distance of two or three inches. Through this interspace the shale or coal falls, touching on its way the red-hot walls of the cylinder. The volatile products are removed by two large conduits, one near the base, the other at about the middle of the cylinder. Holmes's retort is in principle similar. In some horizontal retorts, more especially adapted to utilise

"small" material, a hollow rotating screw is used to urge the shale forward; in others a chain is employed. On account, however, of the difficulty with which heat traverses small shale, such processes, especially when mechanical power is used, must involve considerable expense. Hollow cylinders, moreover, suddenly expose the whole of the shale to great heat, and the yield of solid paraffin is then materially reduced.

Horizontal retorts yield lighter oil (sp. gr. ·84—·86) but less paraffin than vertical retorts, the oil from which is of about ·89 sp. gr.

Heat is applied directly and laterally from below, to six, three, or fewer retorts at the same time. The fuel consists of coal, spent shale being too poor to burn profitably, and coke not yielding the length of flame required, more especially for vertical retorts. The exit-tubes from the retorts are 4—8 inches in diameter, and feed into a main; this may or may not be cooled, and may or may not be connected with a tar-tower to condense very volatile products. From some position in this main, the gas always formed is led off; from 11 per cent. shale, about 9,000 cubic feet per ton are obtained. The liquid distillate is collected in large tanks, which are sometimes steam-jacketed, sometimes not; the latter is the English practice. Here the ammoniacal water settles to the bottom. In order to accelerate the process of separation, various salts have been tried (*e.g.*, sodic chloride and sulphate), as in the extrusion of essential oils from plants; but these have been abandoned on account of their cost, and the cost of recovery. A temperature of 50° C., imparted by a steam-jacket, answers very well; or the distillate may be imperfectly cooled. As a rule, the operation is left to itself.

(*a*). *Watery Liquor.*—This, which constitutes about

one-third of the bulk of the crude distillate, is pumped out as a lower layer after cooling and subsidence; it is maintained at a uniform sp. gr. of 1·03 (6° Tw.) by passing through the gas-scrubber, distillation, another transit through the scrubber, etc., etc., thus never requiring to be discharged from the works, so as to pollute a contiguous stream. The liquor contains, in addition to ammonia, pyridine and similar amines in the caustic state, and as carbonate, sulphide, cyanide, and sulphocyanide. The shales worked in this country may be regarded as furnishing, on the average, ·08 per cent. of ammonia; and we may estimate this at about half the amount theoretically attainable, the spent shale still retaining a small weight of nitrogen. The ammoniacal liquor is introduced into horizontal cylindrical stills, capable of holding 1,000—3,000 gallons; it is heated either directly or by means of an interior steam-coil, so as to fractionally distil off the ammonia. Lime is sometimes added before boiling, sometimes after partial boiling, but often not added at all; it should, however, be, as a rule,* employed, so as to prevent the appearance of cyanides in the distillate. Ammonic cyanide, in presence of air, rapidly corrodes iron fittings, and the sulphate afterwards prepared has a distinct blue colour, owing to the presence of ferric ferrocyanide (Prussian blue). Olive oil and charcoal have both been used as purifiers of the gaseous ammonia; but the former absorbs ammonia to little purpose, the latter oxidises it to nitrate; the proper purifier is lime placed in the still. The gaseous ammonia, with some steam, passes onward, in some works, through a condenser and wash-bottle to a lead-lined trough, the back of which is screened by a curtain inside; the curtain is parallel to the front of

* An exception to this is when the spent liquid has to be afterwards passed through scrubbers, which lime is apt to foul.

the trough, which is closed behind it, but open in front of it. The bottom of the trough slopes somewhat towards the front. The ammonia and steam enter behind the curtain, and encounter oil of vitriol of sp. gr. 1·4 (80° Tw.); crystals of ammonic sulphate soon form, and are removed in perforated ladles. The vitriol, which must be prepared from pure sulphur, is renewed from time to time, as soon as a smell of ammonia is perceived, or the scum becomes brown. The crystals are dried by mere draining; they then contain a little free hydric sulphate, with traces of uncrystallisable pyridinic sulphates, and some water. They could undoubtedly be decidedly improved by the use of the centrifugal machine. Rigorously pure ammonic salts cannot be prepared by any direct process from the watery liquor. Sulphate prepared from liquor obtained in the low-temperature process is less liable to organic impurities than that which is similarly prepared from ordinary gas-liquor.

(β). *Oily Liquor or tar proper.*—This is pumped into cast-iron stills holding about 250—2,000 gallons, and protected beneath by perforated brick arching, so that the heat plays round the side of the still rather than on its base. Gaseous hydrides first come off, and are caught in a tar-tower; some ammonic sulphide generally accompanies them. At and near 100°, some strong ammoniacal liquor and light oil pass over; after this the temperature rises rapidly, and may exhibit an approximately stationary point. The operation is pushed to dryness, and furnishes a vesicular coke, very free from sulphur and ash, and worth on those accounts about 24*s.* per ton. During the earlier part of the process, the condenser, which, like most large condensers, is separated from the still by a wall, is cooled by a stream of cold water; but as soon as the distillate becomes so rich in paraffin as to solidify, the worm is allowed to heat up.

The worm is made of lead. Water comes over during nearly the whole of the distillation, but especially towards the close, when a new destructive distillation of oxygenous pitch occurs. The residual coke amounts to 5—20 per cent. of the tar.

The mixed distillates (for the paraffin magma is generally added) are now stirred with 2 per cent. of caustic soda, in order to take up phenol and its analogues ("kreasote"), acetic bodies, and, perhaps, some terpenes; the sodic extract is drawn off below, and the supernatant fluid, after washing with water, is agitated with 5 per cent. of oil of vitriol of sp. gr. 1·7 (140° Tw.).

10. This latter liquid has but little action on the fatty hydrides proper; but on hydrides containing less hydrogen, it acts powerfully, resinifying and polymerising them as it does turpentine. Schorlemmer has isolated three of these polymers from cannel paraffin oil; he finds them to have the formulæ $C_{12}H_{20}$, $C_{14}H_{24}$, and $C_{16}H_{28}$ respectively, corresponding to a range of 210°—280° in boiling-point. These are polymers of acetylene, $(C_nH_{2n-2})_2$; before the action of the oil of vitriol, they have half the above formulæ. Now, fatty hydrides or paraffins proper have the general formula C_nH_{2n+2}. It may fairly be presumed that crude paraffin oil contains several orders of degraded paraffins; the whole of them are summarised in the general expression C_nH_{2n-x}, x being 0 or an even number. They should evidently be treated with some hydrogeniser, not with oil of vitriol. (Comp. § 5.)

The mixture of soda or vitriol with the crude oil generally takes only a few minutes; but the subsequent separation of the lower layer may take several hours, especially when the oil is heavy. The action of the soda is sometimes aided by a steam-jacket. Not unfrequently, the soda and vitriol are added in three

successive alternate positions with intervening distillations. The mixing tanks are of very varied capacity, and have been constructed to hold as much as 8,000 gallons; mixture is effected by means of rotating vanes, carried on a vertical axle.

11. The "soda-tar" is treated with carbonic dioxide under pressure: this sets free the "kreasote," and the heavier aqueous hydrosodic carbonate is run off and recausticised with lime. The "vitriol-tar" is distilled with lime or chalk, or even with the soda-tar, to recover the acetylenic polymers and the like above referred to, or diluted with hot water, whereby those polymers are raised to the surface, the lower layer of weak vitriol being used for making superphosphate.

The refined tar is fractionally distilled. The more volatile portions (sp. gr. 0·77—0·63) * are used by painters as a substitute for turpentine, by indiarubber manufacturers as a solvent, and by paraffin manufacturers themselves as a medium from which to crystallise paraffin. The succeeding fractions (sp. gr. 0·83—0·89) are sold as illuminating oil ("paraffin oil").

The next distillate solidifies on cooling, yielding brown crystals of hard paraffin, whose mother-liquid is "blue oil," whence more, but soft, crystals can be obtained by artificial refrigeration.

Crude paraffin may be purified by two meltings with 10 per cent. of oil of vitriol (more heat being applied on the second occasion); there is an intervening pressure of the cake, and it is finally melted with aqueous caustic soda. The more general process consists in dissolving the paraffin in about an equal bulk to as little as 10 per cent. of the light paraffin oil, crystallising, and pressing very

* Mr. Coleman now obtains a further quantity of very volatile hydrocarbides by compressing shale gas.

strongly; this is done thrice at least, with a pressure after each crystallisation, the solution being sometimes filtered through animal charcoal and paper, and finally steamed. Carbonic disulphide (10—20 per cent.) has sometimes been used as a solvent instead of light paraffin oil.

The products which leave the retort after the solidifiable paraffin, are thick or buttery. These are sold, with little purification, for lubricating purposes, with or without addition of vegetable oil.

12. Solid paraffin is used chiefly for making candles, for which it is admirably fitted, by reason of the great luminosity with which it burns. The softer kinds, when dissolved to saturation in naphtha, and mixed with about 5 per cent. of vegetable oil, are, as Stenhouse has shown, excellent waterproofers of cloth, linen, indiarubber hose, leather, and other fabrics, to which they also impart greater tensile strength.

13. The accompanying statistical table of annual working comprises the returns made by twenty Scottish manufacturers to the Rivers Pollution Commissioners (1872).

Paraffin Oil Manufacture (1872).

Shale.	Vitriol.	Caustic Soda.	Steam.	Coal.	Crude Paraffin.	Illuminating Oil.	Paraffin.	Blue Oil.	Lubricating Oil.	Ammonic Sulphate.	Refuse Shale.	Salmiac.	Naphtha.
Tons.					Gal.	Gal.	Tons.	Tons.					Gals.
70,000	260	20	117	10,000	460,000	250,000	80	130	..	60	..	..	..
21,000	500	200	25	8,000	..	400,000	150	..	130,000	..	..	..	..
30,000	100	..	80	7,000	950,000	..	..	..	..	100	24,000	..	..
13,000	15	..	18	3,500	350,000	..	..	..	..	15	20,000	..	..
42,000	150	..	..	13,000	1,050,000	..	..	..	..	200	..	..	..
7,000	200	30	30	6,000	240,000	180,000	50	..	30,000	..	4,000	..	..
2,000	80	10	10	1,000	65,000	30,000	..	..	10,000	..	..	3	..
[Cannel 7,317]	481	71	20	3,000	708,281	252,534	17	68,376 (?)	99,612	..	..	..	17,742
45,000	800	65	400	30,000	102,800	635,000	..	..	305,000	350	38,000	..	..
3,500	6	..	..	1,200	145,000	..	..	..	..	6	2,600	..	..
8,500	50	..	10	5,000	250,000	..	..	..	..	..	3,000	..	..
..	340	120	40	1,400	1,000,000	460,000	120	..	450 tons.	..	..	..	14,000
6,708	430	80	54	5,500	450,000	180,000	100	..	58,000	230	5,000	..	120,000*
6,000	12	..	12	4,000	240,000	..	..	..	..	30	4,000	..	..
[Cannel 20,000]	340	50	40	2,400	..	208,000	53	..	500 tons.	36	14,000 coke.	..	21,000
..	110	40	18	700	..	45,000	45	..	5,000 gals.	..	..	..	..
38,500	500	125	..	24,000	..	1,000,000	500	..	120,000 „	250	32,000	..	40,000
[Cannel 3,400]	300	80	40	5,500	20,000	50,000	..	..	150,000 „	..	..	..	2,000
236,379	4,790	766	120	40,000	..	1,500,000	1,000	..	250,000 „	130	40,000	..	150,000
134,000	2,940	628	280	73,210	..	2,285,400	1,300	..	172,000 „	585	11,000	..	120,000

* ? Partly coal tar.

Omitting the figures relating to cannel, we have the following results, calculated (I) from the percentages given by corresponding returns, (II) from (I) and the total shale.

	I.	II.
Total shale	100·00 tons.	663,587 tons.
Spent shale	34·73 „	230,464 „
Coal	34·87 „	231,393 „
Caustic soda	·343 „	2,276 „
Oil of vitriol	1·63 „	10,826 „
Steam	·20 (H.P.)	1,327 (H.P.)
Crude paraffin..	3·20 tons.	21,235 tons.
Illuminating oil	·4424 „	2,936 „
Lubricating oil	·880 „	5,842 „
Blue oil	·19 „	1,261 „
Naphtha	·37 „	2,455 „
Ammonic sulphate	·32 „	2,123 „
(Equal to ammonia	·08) „	535 „

The "horse power" does not probably include that which is required at the pits. The mean results above given are probably too low.

14. Paraffin is a mixture of neutral, non-oxygenated bodies, and contains about 85 per cent. of carbon to 15 per cent. of hydrogen. Its constituents are the "fatty hydrides" of which mention has already been made. This point was first conclusively proved by Gill and Meusel, who found that when excess of paraffin is heated with bromine in sunlight for some time, half the bromine is converted into hydric bromide.

$$C_nH_{2n+2} + Br_2 = C_nH_{2n+1}Br + HBr.$$

This reaction is characteristic of hydrides. The same chemists found paraffin to yield cerotate ($C_{27}H_{54}O_2$) when oxidised with chromic mixture. Their sample, then, which melted at 56°, consisted chiefly of cerotylic hydride $C_{27}H_{56}$. The softer and more fusible paraffins are doubtless mainly composed of lower hydrides. Galletly has isolated a shale paraffin melting at 80°.

It is worthy of remark that the "aromatic" hydrides, C_nH_{2n-6}, occur only in very minute quantities in any of the low-temperature industries.

COAL TAR.

15. Coal tar is formed by the destructive distillation of coal at a high temperature, usually a bright red-heat, or beyond. Although it contains fatty hydrides, they are chiefly liquid ones, and not paraffin. Among its constituents are aromatic hydrides (of which traces only are found in natural or artificial petroleums), their alcohols (occurring in very small quantities in petroleums), and naphthalin (absent from petroleums). Chrysene occurs both in the low and high-temperature oils.

16. If the general formulæ of fatty be compared with those of aromatic compounds, as in the following examples—

	Fatty.	Aromatic.
Hydrides	C_nH_{2n+2}	C_nH_{2n-6}
Alcohols	$C_nH_{2n+2}O$	$C_nH_{2n-6}O$
Olefines	C_nH_{2n}	C_nH_{2n-8}

we observe that aromatic bodies contain eight weights of hydrogen less than the corresponding fatty bodies. Thus is the high-temperature industry, to the extent that it is specially characterised by aromatic compounds, *a dehydrogenising process*.

17. It was formerly the custom to prepare coal tar in

horizontal iron retorts. This method admitted of a comparatively small consumption of fuel under the retorts, which, however, wore out very rapidly. Hence horizontal clay retorts are now almost universally employed. These, on the other hand, require an increased amount of fuel to heat them, and are always worked hotter than iron retorts; moreover, they produce much more naphthalin, which is still almost a waste product, and consequently a diminished quantity of benzol. Nevertheless, I have been recently informed of the existence of a gas-work in which, despite the clay retorts, no appreciable amount of naphthalin is formed. If this be correct, we must attribute the generation of naphthalin not so much to temperature, as to impurities (perhaps sulphur and oxygen) present in the coal distilled.

A clay retort is semicircular in section, having a radius of 18 inches, a length of 9 feet, and a thickness of 2½ inches. It is flanged in front, so as to receive an iron door, which is tightened with wet clay and pressed on by a screw. Five of such retorts can be conveniently heated together; the best working temperature being about 1,100.° The charge is sufficient to fill them to about three-fourths of their capacity. The residual coke is drawn and quenched every three hours (a minimum) to eight hours. By means of an exhausting apparatus, the distillation is kept in process at an average internal pressure of about half an inch of water. Some graphite is always formed, and remains strongly adhering to the inside of the retort.

18. All the products of distillation, after leaving the retort, pass into a "hydraulic main;" here the liquid products are deposited, and thereby separated from the gaseous ones. The bent pipe from the retort dips slightly under the liquid in the main, into which no air consequently passes when the retort is opened.

Purified coal gas contains about ·5 vol. of hydrogen, rather more than ·3 vol. of marsh gas, ·05 vol. of olefines and ·05 vol. of carbonic oxide.

A discussion of the chemistry of the gaseous products of the distillation is reserved, on account of its extent, for a future course of lectures.

The treatment which the crude tar undergoes is remarkably similar to that to which crude paraffin oil is submitted. The liquor is separated from it and treated for ammonia exactly as in the low-temperature industry, and yields about the same percentage return.

Coal yields from 1—2 per cent. of liquor, from 3—6 per cent. of tar, and about 50—70 per cent. of coke (containing 2½ per cent. of ash); the remainder represents the yield of gas, and the working loss (about 10 per cent.). It is usual to distil coal, or such a mixture of coals, as shall yield about 9,000 cubic feet of gas (sp. gr. 0·6) per ton, or about 20 per cent.

19. Modern tar is, as a rule, heavier than the liquor; this must necessarily be the case where napthalin is produced in quantity. It is treated with steam (or distilled with one-fifth of its volume of water, or distilled by the heat of a steam-coil) to remove light naphtha, or crude "benzol." The stills hold from 500 to 4,000 gallons, and are horizontal cylinders. The steam brings over about 10 per cent. at most of light naphtha (sp. gr. 0·78—0·83*), and some ammoniacal water, which is treated like the other "liquor." The residue of the distillation is heated by fire to about 200°, when most of the heavy oil comes over, and afterwards to over 300°. The residual pitch, which amounts to 30—50 per cent. of the tar, is after several hours' cooling (either in the still or a separate tank), run off into moulds; it is generally utilised for

* Formerly this distillate was allowed to reach the sp. gr. 0·95.

"asphalt," by mixture with about four times its weight of sand, chalk, or other inert material.

The light naphtha is run off the "liquor" beneath it, and churned with about 5 per cent. of oil of vitriol, and afterwards with about 2 per cent. of caustic soda (in aqueous solution, of sp. gr. 1·4). Lime may be advantageously used instead of soda, if great care be taken to avoid excess. Sometimes the naphtha is distilled between the acid and alkaline treatment; on the other hand, the lime and acid treatment may be performed, if desired, in the same tank. Mixtures of lime and caustic soda are also used; and this is probably the preferable course. It is also undoubtedly advisable to re-distil the crude benzol before submitting it to this chemical treatment. The residues of this second distillation, when mixed with lime (*see* ROSIN OIL), yield a lubricating "grease," as is the case with several genera of unsaturated hydrocarbides. Finally, the purified benzol is distilled by steam. It then has a sp. gr. of about 0·86.

The heavy or "dead" oil may be used, as such, for preserving or "kreasoting" timber. It is more commonly distilled. The earlier portions of the distillate (150—200°) contain phenol and its homologues ("kreasote"); the following portions (200—212°) are rich in napthalin; and the next fraction (to 360°) yields crystals of anthracene on cooling. Napthalin is not at present utilised on the large scale; but anthracene is the source of artificial alizarin. Tar yields rather less than 1 per cent. of anthracene. The mother-liquid of the anthracene, after further concentration by distillation, and a second deposition of crystals, is chiefly valuable for illuminating and, more especially, for lubricating purposes. The treatment of the phenol fraction is the object of a special industry, that of carbolic acid. There can be little doubt

that the future economical treatment of dead oil, and, in general, crude oils of high boiling-point, will in the main turn upon some method of distillation in vacuo.

20. Annexed is a table of the known products of the destructive distillation of coal. The formulæ, boiling-points, and melting-points are added, so far as known.

Destructive Distillation of Coal.

Name.	Formula.	B.P.	M.P.
Hydrogen	H_2	..	..
Methylic Hydride	CH_4	..	..
Hexylic ,, ...	C_6H_{14}	68°	..
Octylic ,, ...	C_8H_{18}	119	..
Decylic ,, ...	$C_{10}H_{22}$	..	..
Paraffin	C_nH_{2n+2}	..	..
Ethylene	C_2H_4	..	..
Tritylene	C_3H_6	..	..
Pentylene	C_5H_{10}	31	..
Hexylene	C_6H_{12}	71	..
Heptylene	C_7H_{14}	97	..
Acetylene	C_2H_2	..	..
Crotonylene	C_4H_6	18	..
Hexoylene	C_6H_{10}	80	..
Benzol	C_6H_6	80	3°
Parabenzol	C_6H_6	97	..
Toluol	C_7H_8	111	..
Xylols (3)	C_8H_{10}	139	..
Cumol (?)	C_9H_{12}	166	..
Mesitylene	C_9H_{12}	163	..
Cymol	$C_{10}H_{14}$	177	..
Naphthalin	$C_{10}H_8$	218	79
Anthracene	$C_{14}H_{10}$	360	213
Methanthracene	$C_{15}H_{12}$	..	196
Chrysene	$C_{18}H_{12}$	..	249
Retene	$C_{18}H_{18}$	..	..
Pyrene	$C_{16}H_{10}$	..	142
Water	H_2O	100	0
Hydric Sulphide	H_2S	..	− 85
,, Sulphocyanide	HCNS	..	..
Carbonic Oxide	CO	..	..
,, Dioxide	CO_2	−78	..
,, Disulphide	CS_2	47	..
Sulphuric Dioxide	SO_2	−10	..
Hydric Acetate	$C_2H_4O_2$	120	15
Phenol	C_6H_6O	188	35

Destructive Distillation of Coal—(continued).

NAME.	Formula.	B.P.	M.P.
Cresol	C_7H_8O	230°	..
Phlorol	$C_8H_{10}O$	219	..
Rosolic Acid	$C_{20}H_{18}O_4$	..	..
Brunolic Acid	$C_xH_yO_z$	..	..
Ammonia	NH_3	−33	..
Butylamine	$C_4H_{11}N$	75·5	..
Aniline	C_6H_7N	182	..
Cespitine	$C_5H_{13}N$	96	..
Pyridine	C_5H_5N	115	..
Picoline	C_6H_7N	134	..
Lutidine	C_7H_9N	154	..
Collidine	$C_8H_{11}N$	170	..
Parvoline	$C_9H_{13}N$	188	..
Coridine	$C_{10}H_{15}N$	211	..
Rubidine	$C_{11}H_{17}N$	230	..
Viridine	$C_{12}H_{19}N$	251	..
Leucoline	C_9H_7N	235	..
Lepidine	$C_{10}H_9N$	260	..
Cryptidine	$C_{11}H_{11}N$	..	..
Pyrrhol	C_4H_5N	133	..
Hydric Cyanide	HCN	26	..
Fluorene	$C_{13}H_{10}$	302	..
Phenyl	$C_{12}H_{10}$	239	70°
Acenaphthene	$C_{12}H_{10}$	269	100
Phenanthracene	$C_{14}H_{10}$	340	99
Carbon (hydrogenated)	C_n	..	..

The total amount of coal mined in 1874 was about 260,000,000 tons. Of this, the United Kingdom produced about 125,000,000 tons, 8 per cent. of which may be taken as used for gas-making: this would correspond to about 450,000 tons of oily tar.

WOOD TAR.

21. Wood consists essentially of cellulose ($nC_6H_{10}O_5$), water, and a little mineral matter. When heat is applied to it in closed vessels, it decomposes, giving off, among other products, a quantity of steam;* at first, therefore, the process is necessarily under "low-temperature" conditions. As cumulative resolution continues, less water relatively is given off, and the heat can exert its full effect; the second stage of the distillation is therefore under "high-temperature" conditions. Wood thus yields both aromatic and fatty bodies; and these are especially characterised by being to a great extent oxy-compounds, as is natural in a series of cellulose derivatives. These reactions of cellulose show that it cannot be considered, as has often been supposed, a "hydrate of carbon;" certainly not in the sense that slaked lime is said to be a "hydrate of lime." It is very interesting to note, as a further consequence of the mixed conditions of this distillation, that napthalin and paraffin are both present among the products.

22. The heat is allowed to reach bright redness; charcoal is left in the retort, illuminating gas is evolved, and the tar is separated and condensed in a very wide copper worm. Neither sulphur-compounds nor ammonia is given off. Wood may yield, approximately—

Charcoal..	28—30	per cent.
Acid water	28—30	"
Oily (light or heavy) tar	7—10	"
Gas	30—37	"

* Furfurol can be obtained at about 200°, or even lower.

The retort is made of thick boiler-plate, and either horizontal or vertical; the former position is the better of the two. When wood is heated for the purpose of making gas, the retort is followed by a heated empty chamber or "generator," in which takes place what is virtually a second destructive distillation.

The wood should, in any case, be dry. When worked for gas, the charge is about 50—60 kilos., yielding about 16 cubic metres of gas in 1·5 hours. When worked for tar, the charge amounts to one or two hundredweight or more, which are distilled in 12—14 hours, the initial heat being low; in this case, the gas is burned under the retort. The writer has seen in use round cast-iron retorts 1¼ inch thick, 7 feet long, and 3¼ feet in diameter; when worn underneath, these could be re-set bottom upwards, and had been known to last from three to ten years.

Crude wood-gas contains about 40 per cent. of carbonic oxide, 26 per cent. of dioxide, and 11 per cent. of marsh gas. The purified gas contains about ·3 vol. of hydrogen, ·25 vol. marsh gas, ·08 vol. hydrocarbides, and ·3 vol. carbonic oxide. It is 1·2 times heavier than coal gas. which it considerably exceeds in illuminating power, and requires very open burners for its proper combustion.

23. The *watery* portion of the distillate from a ton of wood amounts to 100 gallons, containing 4—8 per cent. of the weight of the wood in "glacial acetic acid" (hydric acetate), and having the sp. gr. 1·03—1·04. This is termed "pyroligneous acid." It is drawn off from below the tar proper (which, however, is frequently beneath it), and may be used at once for making iron mordant, which is a solution of scrap iron in aqueous hydric acetate, and contains ferrous, with some ferric acetate. It is also treated with litharge, in order to prepare plumbic acetate ("sugar of lead"). A better product is, however, obtained by re-distilling the

crude pyroligneous acid, an operation which is conducted in copper stills. The first portion, or 10 per cent. of the distillate, consists of dilute crude *wood spirit* or methylic alcohol (CH_4O); this is used in preparing "methylated spirit" or "finish," a mixture of impure methylic with ordinary alcohol. As the methylic alcohol leaves the still, a quantity of tar which it held in solution separates out. The subsequent acetic distillate has a brownish-yellow colour. It is purified by conversion into sodic or calcic acetate, by saturation with the corresponding carbonate. The resulting solution is evaporated to dryness and roasted to a point just short of decomposition (240° in the case of sodic acetate); this treatment destroys all tarry matter. The residue can now be distilled with hydric sulphate or chloride, either with or without a previous crystallisation from water; the operation is performed in horizontal retorts of cast-iron. If sodic acetate be the salt chosen for treatment with hydric sulphate, the residue in the retort is sodic sulphate, which can be sold to the soda manufacturer. The amount of hydric sulphate or chloride used must depend on the amount of acetate present; but this latter is always kept slightly in excess when hydric chloride is used, so as to avoid the presence of chlorine in the distillate. Calcic acetate requires rather less than an equal weight of aqueous hydric chloride of sp. gr. 1·16. When hydric sulphate is employed, it is difficult to avoid contaminating the product with sulphurous oxide, more especially when imperfectly roasted acetate is used; in this case, there must be a fresh rectification over some oxidiser, potassic dichromate for instance.

24. Hydric acetate, even in the glacial condition, can also be prepared by a process contrived by Melsens. This consists in half-saturating the aqueous solution with potassic

carbonate, evaporating to dryness, and heating to incipient fusion. The residue, which consists of hydropotassic acetate [$KH.(C_2H_3O_2)_2$] is transferred to a retort, and distilled below 300°. The distillate is at first somewhat aqueous, but soon increases in strength, and then solidifies on cooling. The residue in the retort is neutral acetate, which can be evaporated again and distilled with a fresh portion of hydric acetate.

In preparing acetic distillates, the spouts of the retorts and worms must be made of copper. Worms have also been constructed of tin, and even silver; earthenware is not so advantageous.

Little, if any, glacial acetate is now made in this country.

25. The *tar proper* is seldom utilised, at any rate in Great Britain; and much of the Russian wood tar is adulterated with brown British naphtha. On distillation, it yields (at 70—250°) a light oil of sp. gr. ·841—·877. This contains, successively, oxy-products and benzol to 100°; chiefly aromatic hydrides to 150°; more aromatic hydrides and phenol, cresol, &c., together with *oxy*-phenol ($C_6H_6O_2$, a characteristic product), to 200°; then naphthalin and paraffin. Some pitch remains behind. The 150—200° fraction is known as "wood kreasote." The intermediate fatty hydrides seem to be absent; but they are represented, certainly as far as C_{10}, by the corresponding fatty ketates (*acids*) and methylic alcohol.

26. Most woods are available for acetate making; those being (according to Payen) the best whose cells contain most "matière incrustante." Pine wood yields most tar; beech, most liquor. Sawdust can also be used; but it requires to be forced through the retort by means of an endless screw. Peat yields similar products. In Russia, the outer bark of the birch, after stacking, is made to furnish

a green tar; this is used in the treatment of leather, to which it imparts a peculiar smell.

The kreasoting of wood with wood tar was known to Glauber (1657); and the preparation of pyroligneous acid is at least as ancient.

Wood Tar (Appendix).

27. In certain cider districts, presumably French, the marc of apples is destructively distilled. It yields very luminous gas and a yellow tar; the latter turns black on exposure to the air, and is thick, but becomes fluid at 80°. The products from 100 parts of tar are:—

61·5	Water	30·5
	"Benzol"	15·0
	Phenol	8·0
	Kreasote	3·0
	Undetermined carbides, &c... ..	5·0
38·5	Paraffin oil	4·5
	Paraffin	11·0
	Carbon	21·0
	Loss	2·0

ROSIN OIL.

28. Ordinary pine resin or rosin—a French or South American product—is essentially a mixture of hydric pinate with sylvate, both of which bodies have the formula $C_{20}H_{30}O_2$; and it is probable that the corresponding anhydrides are often present. These bodies are perhaps oxidation-products of turpentine or turpentines:—

$$4C_{10}H_{16} + 3O_2 = 2C_{20}H_{30}O_2 + 2H_2O.$$

The destructive distillation of rosin much resembles that of wood ; but it is wholly a low-temperature industry, and can be carried out below 350°, though this temperature is often exceeded. In the now obsolete manufacture of rosin-gas (wherein the distillate was passed through red-hot iron chambers), some naphthalin could be detected in the tar; 100 pounds of rosin yielded about 1,300 cubic feet of crude gas, containing 8 per cent. of carbonic dioxide.

29. The retort consists of a vertical cylinder, about two diameters high, and having a spherical top and bottom. It is charged to within a few inches of the top with rosin; an ordinary charge consisting of about 70 barrels, holding about 25 gallons each.* Direct heat is applied to the bottom of the still; and the entire operation lasts 56 hours. Water passes over throughout the entire operation.

30. The products are:—

60—70 gallons "spirit."
1,600 „ "oil," for grease-making (if fired slow).
6—7 cwt. coke.
40—50 gallons weakly acetic water.

There is very little gas; but it is heavy, and powerfully anæsthetic, containing carbonic oxides, ethylene, and butylene. The layer of coke, containing a good deal of gravel and other mineral impurity from the rosin, is about 6 inches thick.

Furck applies direct heat to the bottom of the retort, drives superheated steam through an upper central coil therein, in order to maintain the temperature, and passes

* The sp. gr. of solid rosin is about 1·075.

steam through the whole mass of rosin. The following are the products:—

Acetic water	.. ..	under 165°
Spirit (15 per cent.*)	..	—
Oil (25 per cent.) ..	..	„ 290
„ (25 per cent.) ..	..	„ 315
„ (12½ per cent.) ..	..	„ 350

The residue in the still is liquid, and is run off through a cock.

As manufacturers generally avoid, as far as possible, the production of "spirit," distillation without steam is ordinarily preferred.

31. The nature of the distillate is but little known. Benzol and toluol have been found in minute proportions in the products of the steam process; but the characteristic feature is a series of C_{10n} bodies, directly related to turpentine and to the original rosin, just as the hexylic hydride (C_6H_{14}) of petroleum is related to its present cellulose ($nC_6H_{10}O_5$).

32. Some thirteen years since, at the request of the late Prof. Thomas Anderson, I made a partial investigation of rosin oil. A fraction from the "spirit," boiling pretty constantly at 154—156°, had the sp. gr. ·853 at 14·4°, and almost exactly the composition of turpinol $(C_{10}H_{16})_2.H_2O$. The turpinol of Wiggers and List is said to have the sp. gr. ·852, and to boil at 168°. Their product gives a crystalline hydrochloride $C_{10}H_{16}.2HCl$, but rosin turpinol does not appear to do so. When rosin turpinol is treated with strong oil of vitriol, it yields a liquid having the odour of terebene. When treated with bromine, it furnishes an oily product, containing from 31—43 per cent. of the reagent; chlorine is similarly taken up to the extent of

* Reckoned on the volume of the rosin.

50 per cent.; hydric chloride, to the extent of 18—19 per cent. Another fraction, boiling at 188—193°, and dried over sodium, agreed in composition very closely with turpentine, but it could not be made to yield a solid hydrochloride. From these experiments it would appear that the order of this destructive distillation is (1) acetate, (2) turpinol, (3) turpentines. The spirit, however, contains a remarkable fraction of constant low boiling-point, consisting of a highly hydrogenised compound; when this is distilled with aqueous hydric iodide, it produces a polymerised turpentine, and another compound not yet examined.

[The long white crystals which separate from undried rosin oil, especially the fraction 154—165°, on long standing, were found to have the formula $C_{18}H_{36}O_5$.

	Found.*	$C_{18}H_{36}O_5$.
Carbon	64·69	65·06
Hydrogen	11·23	10·84
Oxygen	24·08	24·10
	100·00	100·00

Kingzett's researches have shown that hydric peroxide is formed in moist oils of the turpentine class, under the conditions named. The generating equation may therefore be:—

$$\underbrace{C_{20}H_{34}O}_{\text{Turpinol.}} + H_2O_2 + 3O_2 = \underbrace{C_{18}H_{36}O_5}_{\text{Crystals.}} + 2CO_2.$$

The crystals begin to sublime at a little above 100°, but at a lower temperature when moist. They are very readily soluble in cold water, alcohol, and ether, and melt

* Mean of three very concordant analyses of three different specimens.

at 106·7.° They do not absorb bromine-vapour, and do not seem to furnish oxalate on treatment with hydric nitrate. Neither the aqueous nor the alcoholic solution gives a precipitate with polyplumbic acetate. The crystals give an orange-red coloration with strong oil of vitriol in the cold.]

Rosin "spirit" has been used as a substitute for turpentine in painting, varnish-making, and currying.

33. Both rosin "spirit" and "oil" have the property of combining with alkaline and other hydrates to form peculiar greasy bodies; which, again, can hold together, in the form of a buttery mass, an enormous excess of hydrocarbide. This phenomenon is mainly owing to the "unsaturated" character of the turpentines, one of their oldest recognised chemical properties. Synthetical experiments carried out in my own laboratory, show that the following turpentine mixtures—

$$C_{10}H_{16}+2CaH_2O_2$$
$$C_{10}H_{16}+NaHO$$
$$C_{10}H_{16}+KHO$$

furnish what are probably real chemical compounds of these; the first solidifies in a few minutes; the second, in a few days; the third, after a longer period. The minimum ratio in the "rosin grease" of commerce is about $13(C_{10}H_{16}) : CaH_2O_2$; so that the original calcic compound is capable of converting at least 18 times its weight of liquid hydrocarbide into "grease."

In the actual preparation of rosin grease, a small portion is rapidly stirred with about three-fourths of its weight of slaked lime made to a cream with water. The oil and hydrate quickly unite, extruding the superfluous water, which is at once run off; the solid compound is then diluted with more oil, and the solution stirred into a further final quantity, until the total dilution already mentioned is

attained. The whole operation takes about half an hour.

Rosin grease is used as a lubricant for iron bearings, and especially for the axles of pit-waggons, which are much exposed to moisture. On account of the rapidity with which it acetifies under the influence of heat and friction, it is not adapted for brass bearings. As ordinarily sold, it nearly always contains a kindred grease, made from the unsaturated coal-tar hydrocarbides which are left when crude benzol is rectified. In Glasgow, there are about a dozen rosin oil stills.

34. The purification of rosin oil is generally effected, if at all, by treatment with lime-water to remove acetate, and redistillation with, or without, a current of steam. The use of oil of vitriol is inadmissible, because it polymerises and chars such hydrocarbides. The most appropriate treatment that suggests itself is, distillation over an alkaline reducing agent in a current of steam.

Appendix to Rosin Oil.

CAOUTCHOUC.

35. When caoutchouc ($nC_{10}H_{16}$) is submitted to a temperature of about 316° in a close vessel, it yields a very light volatile distillate, and a residual mass which furnishes a good varnish when dissolved in oil. The distillate consists of isoprene (C_5H_8), together with caoutchin ($C_{10}H_{16}$) and other polymers of the terpene group; rectification is performed with the aid of steam. It soon turns brown in contact with air, especially if water be present. It is said to have the peculiar property of dissolving copal without the aid of heat, and readily takes up many resins and oils.

PETROLEUM.

36. Petroleum is a natural mixture, chiefly of fatty hydrides; it proceeds from an unknown source, and is most abundantly found in the upper Devonian and carboniferous limestone of the United States and Canada. It occurs in all parts of the world, and, like coal, is probably not confined to any one geological formation. It is apparently in most cases produced by the long-continued application of a gentle heat to some derived form of cellulose; for if the temperature were a high one, gas must be evolved from the soil in more places, and in far greater volume, than is ever found to be the case.

The method of winning is by means of wells, from 500 to 1,000 feet in depth.

37. Petroleum contains in solution both hydrogen and the fatty hydrides C to C_5, which are gases or vapours under ordinary conditions; these latter were detected by Ronalds and Fouqué. The liquid terms C_5 to C_{15} were isolated by Pelouze and Cahours, and by Schorlemmer; solid paraffins are also present, in amount increasing with the density. The last chemist found traces of benzol and its homologues (aromatic hydrides). It is probable, moreover, that unsaturated fatty hydrocarbides are contained in petroleum. Of the above constituents, hexylic hydride C_6H_{14}, a substance closely related to cellulose, $nC_6H_{10}O_5$, is the most characteristic; this was also found by Greville Williams in boghead cannel oil.

38. Native petroleum is always more or less coloured, and requires refining with caustic soda and vitriol, just as is the case with artificial petroleum. Sp. gr. 0·8—0·9. American petroleum is distilled prior to export, in order to remove the dissolved gaseous hydrocarbides, which, if allowed to escape into the air, would furnish a readily inflammable

and explosive mixture. The processes of purification present no peculiar features. The purified products are divided into four classes, viz. (1) very light oil of sp. gr. 0·7 and under, used as an anæsthetic, and for "carbonating" gas and air; (2) oil of sp. gr. 0·7—0·8, used for burning in sponge lamps; (3) paraffin oil of sp. gr. 0·8—0·9, for ordinary illuminating purposes; and (4) lubricating oil containing paraffin.

The total amount of illuminating oil is about 80 per cent. of the purified distillate.

Muspratt examined Canadian petroleum, with the following results:—

Light coloured naphtha (sp. gr. ·794)	20
Heavy yellow naphtha (sp. gr. ·837)	50
Lubricating oil rich in paraffin ..	22
Tar	5
Charcoal	1
Loss	2
	100

The paraffin amounts to about 3 per cent.*

Canadian oil is more difficult to purify than the American kind.

Petroleum and its waste products are themselves destructively distilled, in the United States, for gas.

Petroleums vary very much. The best and safest guide to their composition and usefulness is a knowledge of their specific gravity.

39. The regular importation of American petroleum into Europe commenced in about 1859. It has since increased at so enormous a rate as to reduce the price of artificial petroleum from about 2*s.* 6*d.* to 9*d.*, or even less, per gallon.

* The American oils contain less paraffin.

Probably, however, the maximum of supply from the natural source has now been reached, and the European industry may be expected to revive.

The export for 1871 amounted to 154,877,377 gallons, mostly proceeding to Germany alone; and it is inevitable that this vast flow must ere long be exhausted.

Appendix to Petroleum.

40. Some of the natural petroleums deserve more especial mention. Thus, for example, *Rangoon tar* is a heavy variety, semi-solid with paraffin, of which it contains about 10 per cent. Illuminating oil can be obtained from it by the transmission of low-pressure steam; paraffin and lubricating oil by higher heating. The distillates are purified by the successive action of caustic soda and oil of vitriol. The light oil has a sp. gr. 0·62—0·86, and boils at 27°—200°; it amounts to about 25 per cent. of the tar. The natural tar is in use as a lubricant; but its entire consumption is at present exceedingly small. The yield amounts—or can amount—to 412,000 hogsheads annually.

De la Rue and Müller distilled crude Rangoon tar in a current of steam (which was superheated when the boiling-point rose above 100°), and obtained the following fractions:—

Below 100°	..	11	Light oils.
110°—145°	..	10	
145°—360°	..	20	
About 360°	..	31	Heavy oils, containing much paraffin.
Above 360°	..	21	
		3	Pitch.
		4	Coke.
		100	

41. There are several petroleum springs on the shores of the Caspian Sea, more especially in the neighbourhood of Apscheron and Bakow. There are also solid deposits of *naphthagil* or *neft-gil,* which resembles bitumen, and has been worked for light oil and paraffin. The natural naphtha has the sp. gr. 0·87, and boils at about 235°; it has sometimes been received colourless from the springs. Neft-gil yields about 15 per cent. of crude paraffin, and 40 per cent. of illuminating oil; but the yield sometimes amounts to 40 per cent. of paraffin.

42. *Native asphalt,* or *bitumen,* is solid at the ordinary temperature. It appears to be formed by the oxidation of the unsaturated hydrocarbides in petroleum. The most remarkable deposits are in Cuba and Trinidad, the asphalt from which islands has been found to yield 1·75 per cent. of paraffin. Other noted localities are the Dead Sea, Seyssel (France), Limmer, and the Val de Travers. Asphalt, being, like resin and terpenes, somewhat acid towards lime, is frequently retained in limestone rocks, or contains much lime. It is in great request for paving purposes.

43. *Ozokerite, Ceresin,* or *Mineral Wax,* is also solid. It occurs naturally in Gallicia, and on the Caspian; but the former locality is of greater importance. The oil-bearing strata, consisting chiefly of salt sandstone and argillaceous schist, occur on the north and north-eastern slopes of the Carpathian Mountains, in a breadth of four to fourteen miles, from Linianowa in the west to Bukowina and Moldau. In Boryslau (Moldau) 325,000 cwt. were produced in 1870, and the total value of the Gallician production for that year is stated at 6·8 million marks. The pits do not exceed 300 feet in depth, and are easily worked; they contain petroleum—exactly similar to the American kind—pasty mixtures of this with ozokerite, and ozokerite proper.

This last is a soft scaly mass, having an odour of fatty hydrides, and the colour of dark beeswax; it is frequently more or less steamed or otherwise heated before export, to ensure greater solidity, and remove earthy impurities. In the crude state, it has been in use for many years at Boryslau for the manufacture of a very inferior quality of candle; the production of white candles from this source dates from a comparatively recent period.

44. When ozokerite is distilled, it furnishes both solid and liquid products, some portion of its paraffins doubtless passing over unchanged. Gintl obtained the following results with Gallician rock-oil:—

	West Gallicia.	East Gallicia.
Very light oil	20	20
Light oil..	50 (sp. gr. ·824)	50 (sp. gr. ·864)
Heavy oil	10	..
Paraffin..	..	8
Hard pitch	10	8
Loss..	10	14
	100	100

It would appear from these numbers that the ozokerite of East Gallicia is likely to contain, on the whole, more solid paraffin.

There are many refineries of ozokerite and ozokerite oil in Austro-Hungary, where the latter is largely used. Ozokerite oil is refined in the same manner as native petroleum; solid brown ozokerite is refined by processes not hitherto completely divulged. These consist, so far as is known, in (1) distillation, usually without steam; (2) treatment of the solid distillate with oil of vitriol (soda being seldom required) and washing with water; (3) crystallisations from the light oil, in presence of animal charcoal. In this last operation, the melted ozokerite may

be preferably melted with animal charcoal, in the absence of a solvent, and the use of magnesic silicate has been patented as an efficient substitute for charcoal. Ceresin is said to be ozokerite bleached without distillation. Native ozokerite yields approximately :—

Petroleum	25
Lubricating oil	21
Paraffin..	36
Coke	8
Pitch and loss	10
	100

Having regard to the fact that native ozokerite is chiefly worked for the purpose of obtaining solid paraffins, distillation in a vacuum might obviously be advantageous; this would be facilitated by the circumstance that little or no gas is given off in the process. Crude ozokerite, as ordinarily distilled, contains chrysene, but not napthalin. The still holds about three tons.

45. Ozokerite, after purification for candle-making, melts at about 61°, is quite odourless and colourless, and has a waxy section. The kind prepared by Otto, of Frankfort-on-the-Oder, is said to melt at 83°, and to be so hard as scarcely to yield to the finger-nail.

PEAT.

46. Peat consists of the "cumulatively resolved" fibrous parts of certain mosses and graminaceæ. It gradually darkens from brown to black with increasing age. Judging from Dr. Angus Smith's results, it grows at the

rate of about an inch in the year. A pectinous substance has been found amongst its constituents. As a fuel, it is most economically used at the spot where it is grown. It has been, however, destructively distilled at a low temperature, for tar, a branch of industry now scarcely profitable. The process gives a very porous, friable charcoal, possessed of great decolorising power; gas rich in carbonic dioxide is also given off. A ton of good peat may yield more than 5,600 cubic feet of gas. The purified gas contains about 11 per cent. of vaporised hydrocarbides, 37 per cent. of marsh gas, 31 per cent. of hydrogen, and 19 per cent. of carbonic oxide; it is thus (as its mode of formation suggests) less oxygenated than wood gas, but more oxygenated than coal gas.

The liquor is rich in hydric acetate.

47. Good peat yields about 6 per cent. of tar proper, which is comparatively easy to purify by the usual method. According to Vohl, 100 parts of peat tar from six sources furnished, on the average, 20·1 per cent. of paraffin oil (sp. gr. 0·82), 21·8 per cent. lubricating oil (sp. gr. 0·86), and 3·4 per cent. of paraffin. This last estimate seems doubtful. Wagenmann found, as a mean, 2·1 per cent. of paraffin; Kane and Sullivan, about 1 per cent.; other experimenters have obtained from 0·75 to 0·5 per cent.

48. Peat yields from 5 to 50 per cent. of ash, one-third of which may consist of ferric oxide. To this source may not improbably be due the occasional ferruginous character of peaty waters, and the decolorising power of peat charcoal.

BROWN COAL OR LIGNITE.

49. Brown coal is intermediate between wood and coal proper, which latter it succeeds in geological time. It sometimes retains the fibrous structure of wood, has a yellow or brown colour, and pasty consistence, and is easily fusible; at others it is quite black, and closely resembles coal. The better kinds retain much moisture.

50. Brown coal has been worked for many years at Weissenfels, in Saxony, where it has yielded, by the ordinary treatment, the ordinary products of the low-temperature process. At these works, according to a report of Dullo (1862 ?), the brown coal furnishes 17·8 per cent. of buttery tar, which yields 20 per cent. of paraffin, and 43 per cent. of illuminating oil. The means of Vohl's more recent figures, which refer to thirteen sources, are—18·6 per cent. of paraffin oil (sp. gr. 0·82), 32·4 per cent. of lubricating oil, and 4·1 per cent. of paraffin—reckoned on the tar.

The above numbers refer to distillates obtained in horizontal cast-iron retorts. If steam be introduced during the process, the tar yields, it is said, as much as 30 per cent. of paraffin.

The product is purified with some difficulty from sulphur and nitrogen.

Although brown coal in many respects resembles peat, it much surpasses that substance in the value of its products of destructive distillation, furnishing, in fact, about three times as much tar, and three times as much paraffin as peat.

51. Such of the brown coals as most closely resemble wood, contain but little nitrogen, and yield, of course, an acid distillate; such as are akin to coal, give an alkaline distillate, being more nitrogenous.

[According to Albrecht, the brown coal industry yielded in 1871 about 4,921 tons of paraffin, and double that weight of illuminating oil. He also states that a ton of medium quality yields 60—65 per cent. of finished products, consisting of:—

15—17	per cent.	paraffin.
28—35	„	illuminating oil.
10—15	„	heavy oil.
2— 4	„	creosote.
4— 6	„	pitch.]

BONE OIL.

52. Bones consist of about two-thirds mineral ingredients, not altered by heat (tricalcic phosphate), and one-third osseine, which is destroyed by heat. The latter substance has the following composition:—

Carbon	50·4
Hydrogen	6·5
Nitrogen	16·9
Oxygen	26·2

Thus bones yield about 6 per cent. of nitrogen. When they are soaked for several days in dilute hydric chloride, their calcic salts dissolve, leaving a mass of flexible osseine, which retains the shape of the original bone.

Osseine dissolves in boiling water, being thereby transformed, without change of composition, into an equal weight of gelatine; hence it is an isomer or polymer of gelatine. In the destructive distillation of bones, it is the osseine alone that furnishes distillate. The manufacture

of bone oil is an industry that survives from mediæval times.

53. The bones are submitted to a preliminary treatment in order to remove fat. This is effected by prolonged contact with hot water, or, much better, by steaming in vertical cylinders. The cylinders hold about five tons of bones, and the operation of steaming lasts about twelve hours. At the end of that time, cold water is admitted from below in quantity more than sufficient to cover the bones; the fat is thus brought to the surface, and is then skimmed off. During the operations of steaming and watering, some gelatine solution is of course formed in the cylinders; this is removed, concentrated, and sold as "glue substitute."

54. The bones are preferably distilled as thus saturated with moisture; dry bones furnish a partially solid distillate, which would inevitably choke an exit-pipe of moderate length. The distillation is performed in horizontal cylindrical retorts made of cast-iron; a convenient size is 9 feet long by 1½ feet in diameter. The retort is completely filled with its charge, and then closed after the fashion of a gas-retort. It is next heated to the lowest possible degree of redness, during eight hours. The residue in the retort consists of "animal charcoal" or "bone black;" this consists, approximately, of:—

Charcoal	10
Calcic phosphate ..	84
Calcic carbonate ..	6
	100

According to some authorities, it invariably retains nitrogen, in greater proportion as the temperature has been lower.

Seven retorts can be heated at one time.

Another and less manageable method is applied to the distillation of dried bones. The retorts, preferably five in number, are charged as before, and their distillate conducted while gaseous, and through a very short exit-pipe, into rectangular leaden chambers. Here a great deal of the ammonic carbonate solidifies; it is purified by sublimation.

55. Both methods furnish a liquid distillate, containing, as in the case of coal, an aqueous and an oily portion. The aqueous portion is a solution of ammonic carbonate, cyanide and hydrosulphide, together with methylamine and its homologues, pyridine and its homologues, and pyrrhol. The oily portion is also charged with these, and contains, in addition, fatty nitriles, fatty and aromatic hydrides. The sp. gr. of the oil is about ·945. This product was formerly known under the name of *Oleum animale Dippeli.*

The aqueous distillate is treated for ammonia in the same manner as the aqueous distillate from coal, excepting that weaker vitriol (sp. gr. 1·2) is used, on account of the richness of the ammoniacal liquor. The resulting sulphate is apt to be coloured with pyrrhol-red.

A ton of bones yields 10—12 gallons of oil, and 130—140 gallons of liquor of sp. gr. 1·04. Attempts to purify the oil for illuminating purposes have hitherto resulted in failure. The exhausted ammoniacal liquor has been used as a sheep-dip.

56. In addition to the above products, the destructive distillation of bones furnishes a very decided amount of gas. Unfortunately, this gas contains too much sulphur, and in too intimate a state of combination, to admit of economical purification. It is, however, possessed of very considerable illuminating power, and is therefore somewhat used to light the more open parts of works, but the greater part

of it is burned under the boilers or retorts. Bone oil is easily utilised in the same way.

57. The extent of this industry depends in a great measure upon that of sugar-refining, upon which accurate data do not appear to be obtainable. Some conception of its magnitude may be formed from the fact that for every ton of refined sugar * a ton of animal charcoal is used; the charcoal is then reburned, and used again, thus undergoing a loss of value to the amount of 40 per cent. per annum. A single firm receives daily, from Glasgow, ten tons of bones for conversion into animal charcoal.

Horn, wool, hair, and *leather* yield a liquid distillate, very similar to that from bones.

SUMMARY.

The application of heat to cellulose leads to the cumulative resolution of that body, and the process is in principle the same, whether performed by nature or by human contrivance. At each stage in such resolution, peculiar products are given off. At a high temperature, the liquid distillate is characteristically "aromatic;" at a low temperature, "fatty."

Inasmuch as a chemical equivalent for much of the "temperature" can be found in "time," we are not surprised at discovering petroleum in rocks never actually igneous; or degraded hydrides, such as turpentine, with other "aromatic" compounds, in living trees.

* It is estimated that about 3,500,C00 tons of raw sugar were produced in 1870.

APPENDIX A.

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APPENDIX B.*

Weights and Measures.

Foreign.		English.
Centimètre	=	0·39371 inch.
2·539954 centimètres	=	inch.
Mètre..	=	39·37079 inches.
„	=	3·28090 feet.
„	=	1·09363 yards.
0·304794 mètre ..	=	foot.
0·914383 mètre ..	=	yard.
Litre..	=	0·220097 gallon.
4·543458 litres ..	=	gallon.
Gramme	=	15·43235 grains.
0·064792 gramme ..	=	grain.
Kilogramme	=	2·204621 pounds (lbs.)
0·453523 kilogramme	=	pound.
50·802377 kilogrammes	=	hundredweight (cwt).
1016·04754 kilogrammes	=	ton.
Kilogramme	=	·0009842 ton.
Centner	=	110·231 pounds.

Temperature.

$$\text{Deg. C.} = \tfrac{5}{9}\,(\text{Deg. F.} - 32).$$

Specific Gravity.

$$\text{Sp. gr.}\dagger = \frac{\text{Deg. Twaddell} \times 5 + 1000.}{1000}$$

$$\frac{\text{Sp. gr.} \times 1000 - 10}{5} = \text{Deg. Twaddell.}$$

* Compiled chiefly from the tables of Mr. Delarve.

† Water being taken as 1,000.

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